

<b>REPORT DOCUMENTATION PAGE</b>			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 1997 August		3. REPORT TYPE AND DATES COVERED Final; 96 Jul - 96 Oct
4. TITLE AND SUBTITLE Evaluation of Post-Treatment Filter, Part 4: Predicted Stack Gas Filtration			5. FUNDING NUMBERS  PR-10262622A552	
6. AUTHOR(S) Mahle, John (ERDEC), and Croft, David (Guild Associates, Incorporated)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ERDEC, ATTN: SCBRD-RTE, APG, MD 21010-5423 Guild Associates, Incorporated, 5022 Campbell Drive, Suites J & K, Baltimore, MD 21236			8. PERFORMING ORGANIZATION REPORT NUMBER  ERDEC-TR-317	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES  This is the last report in this series.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words)  Application of an activated carbon based vapor removal system for stack gas from an incinerator is considered. Several low volatility, highly toxic compounds of great interest for filtration behavior are the polychlorinated dibenzodioxins and dibenzofurans (TetraCDD and TetraCDF). Adsorption equilibria is described by extending the potential relationship into the Henry's Law regime. Design implications for fixed bed and injection technology are reconciled using a CSTR type model to describe reported TCDD and TCDF industrial scale filtration data.				
14. SUBJECT TERMS  Filtration Activated carbon Incinerator stack gas  Henry's Law limit TCDD and TCDF adsorption			15. NUMBER OF PAGES  26	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL	



**EDGEWOOD**

RESEARCH, DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-TR-317

**EVALUATION OF A POST-TREATMENT FILTER  
PART 4: PREDICTED STACK GAS FILTRATION**

John Mahle

RESEARCH AND TECHNOLOGY DIRECTORATE

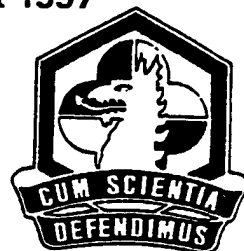
David Croft

GUILD ASSOCIATES, INC.  
Baltimore, MD 21236

August 1997

19971217 018

Approved for public release; distribution is unlimited.



Aberdeen Proving Ground, MD 21010-5423

DTIC QUALITY ASSURED

**Disclaimer**

**The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.**

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 1997 August	3. REPORT TYPE AND DATES COVERED Final; 96 Jul - 96 Oct		
4. TITLE AND SUBTITLE Evaluation of Post-Treatment Filter, Part 4: Predicted Stack Gas Filtration		5. FUNDING NUMBERS  PR-10262622A552		
6. AUTHOR(S) Mahle, John (ERDEC), and Croft, David (Guild Associates, Incorporated)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ERDEC, ATTN: SCBRD-RTE, APG, MD 21010-5423 Guild Associates, Incorporated, 5022 Campbell Drive, Suites J & K, Baltimore, MD 21236		8. PERFORMING ORGANIZATION REPORT NUMBER  ERDEC-TR-317		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES  This is the last report in this series.				
12a. DISTRIBUTION/AVAILABILITY STATEMENT  Approved for public release; distribution is unlimited.		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  Application of an activated carbon based vapor removal system for stack gas from an incinerator is considered. Several low volatility, highly toxic compounds of great interest for filtration behavior are the polychlorinated dibenzodioxins and dibenzofurans (TetraCDD and TetraCDF). Adsorption equilibria is described by extending the potential relationship into the Henry's Law regime. Design implications for fixed bed and injection technology are reconciled using a CSTR type model to describe reported TCDD and TCDF industrial scale filtration data.				
14. SUBJECT TERMS  Filtration Activated carbon Incinerator stack gas  Henry's Law limit TCDD and TCDF adsorption			15. NUMBER OF PAGES  26	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT  UL	

**Blank**

## PREFACE

The work described in this report was authorized under Project No. 10262622A552, Smoke Obscurants/Munitions. This work was started in July 1996 and completed in October 1996.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

**Blank**

## CONTENTS

1.	INTRODUCTION .....	7
2.	LOW CONCENTRATION BEHAVIOR .....	8
2.1	Henry's Law Limit .....	8
2.2	Potential Theory Correlation .....	9
2.3	Analyzing Norit Data .....	14
2.4	Applying Raoult's Law to Post-Treatment Filter .....	19
3.	CONCLUSIONS .....	21
	GLOSSARY .....	23
	LITERATURE CITED .....	25



## FIGURES

1	Representative Isotherm and Henry's Law Slope . . . . .	10
2	Potential Plot for Coconut Carbon . . . . .	12

## TABLES

1	Physical Properties of Adsorbable Species . . . . .	13
2	Measured Adsorption Data from Rordorf . . . . .	15
3	Norit Dioxin Filtration Parameters . . . . .	17
4	Norit Dioxin Filtration Case Results . . . . .	17
5	Case A - CSTR Simulation of Norit Data . . . . .	18
6	Case B - CSTR Simulation of Norit Data . . . . .	18

## EVALUATION OF A POST-TREATMENT FILTER PART 4: PREDICTED STACK GAS FILTRATION

### 1. INTRODUCTION

The disposal of hazardous and nonhazardous waste by incineration is an accepted industrial practice. High levels of conversion to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_x$ , and  $\text{SO}_2$  are easily achieved. However, the chemistry of incomplete combustion also creates trace concentrations of dozens of other components. Post-treatment of the incinerator exhaust is usually provided to remove those noxious species present at the highest concentration. Typically, this involves acid gas scrubbing and particulate filtration. Additional post-treatment processes should also be considered for low-concentration components with high health impact. However, each post-treatment step that is applied contributes additional capital and operating requirements to the facility.

The U.S. Army Program Manager for Chemical Demilitarization is pursuing a plan to destroy the chemical warfare agent stockpile. The United States has constructed an incineration-based facility on Johnston Atoll in the South Pacific. Similar facilities are planned at other sites. The operation of the Johnston Atoll Chemical Agent Disposal System (JACADS) facility is well documented. Analysis of the JACADS stack exhaust has identified the presence of many combustion by-products, all of which are typically found in industrial incinerator exhaust.

To quantify the safety and risk associated with plant operation, a number of processes are analyzed. This analysis is formalized by use of quantitative risk assessment (QRA) and health risk assessment (HRA). Any changes in plant operation can be evaluated using these techniques to assist in the decision-making for further engineering design and plant installation. One such change would include post-treatment technologies, which reduce either accidental or inherent long-term incinerator emissions.

The current demilitarization facilities, JACADS and Toelle, Utah (TOCDF), employ a venturi for particulate removal, a packed bed scrubber tower for acid gas removal, and a mist eliminator. Details of the design can be found elsewhere.<sup>1</sup> In addition to these components, it has been proposed that the stack gases could be filtered for further vapor and particulate removal. A number of concepts exist in various stages of design and development to provide filtration on the flowrate scale appropriate for a chemical demilitarization incinerator facility. Several technologies exist for vapor and particulate filtration. However, for the extremely low concentrations considered here, the available choices are limited.

As part of the JACADS permitting process, a series of RCRA trial burns were conducted with agent feed to the furnaces.<sup>2</sup> The stack concentrations of all the major organic, inorganic, and metal components were quantified. Standard methods were employed for sample collection and analysis.<sup>3</sup> EPA Modified Method Five (MM5) was used to sample for semivolatile products of incomplete combustion (PICs) and dioxin/furans. A

volatile organic sampling train (VOST) was used to collect volatile organics. Samples for metal analysis were collected by a multiple metals train (MMT). These methods collected an integrated sample for the sampling period.

Analysis of the measured trial burn results was performed to identify the major risk drivers.<sup>4</sup> That report also described an adsorption performance prediction model based on earlier reports in this series, Parts 1-3.<sup>5-7</sup> The approach described could be used to model all the components identified in that stack, including all the organics, acid gases, and mercury. However, it might be instructive to consider just the filtration performance against the most important health risk compounds. That report concluded that the risk-drivers for the HRA are the dioxins and furans. Therefore, it is important to consider how those components would behave in a proposed stack gas filter especially at the low concentrations measured in the trial burn reports.

Two components of primary interest are polychlorinated dibenzodioxins and dibenzofurans [tetrachlorodibenzodioxin and tetrachlorodibenzofuran (TCDF)]. The most distinguishing feature of the filtration problem for the dioxins and furans is their low concentration. It is a difficult analytical problem to quantify concentrations in that range, and no adsorption data is available. Therefore, some extrapolation of measured data is required. The assumptions of the model used to make that extrapolation need to be examined and tested. Also, any available data should be consistent with the model.

This work represents the fourth in a series, which has focused on developing a model to predict the performance of a stack gas filter. In addition, experimental results have been reported for low concentration and multicomponent breakthrough. The present study shall address several unique aspects of the stack gas problem, including the appropriate adsorption equilibria for vapor phase concentrations, which are at the detection limit, and the predicted performance for a many-component challenge.

## 2. LOW CONCENTRATION BEHAVIOR

### 2.1 Henry's Law Limit.

At low coverage for a uniform surface, the equilibrium relationship between fluid and adsorbed phase concentrations will be linear. This linear relationship is characterized by a Henry's constant, H, defined as

$$H = \lim_{P \rightarrow 0} \left( \frac{n}{P} \right) \quad (1)$$

where P is the partial pressure, and n is the adsorbed phase loading. The adsorption equilibrium at the lowest coverage corresponds to adsorption predominantly on the highest

energy sites. At high concentrations, the amount of adsorption in the pores,  $q_{sat}$ , is limited by the available pore volume per mass of adsorbent,  $W_o$ , divided by the molar volume of the vapor,  $V_m$ .

$$q_{sat} = \lim_{P \rightarrow P_{sat}} \left( \frac{W_o}{V_m} \right) \quad (2)$$

Ruthven<sup>8</sup> notes that for highly microporous adsorbents, physical adsorption is characterized by isotherms of Type I (concave down), also called favorable isotherms. Adsorption at higher concentrations corresponds to a lower slope of the isotherm. The limiting slope at zero coverage then represents the maximum slope of the isotherm. Figure 1 presents the location of the limiting Henry's law slope versus a hypothetical Type I isotherm. Clearly, the adsorbed phase loading given by extending the Henry's law slope to higher concentrations would always represent a higher loading than that given by the measured equilibrium value.

Ruthven<sup>8</sup> also states that the Henry's constant can be obtained from the limiting slope of experimental isotherms. But, with "strongly adsorbed components it may be difficult to make reliable experimental measurements at sufficiently low pressure to permit the Henry's law constant to be determined directly from the limiting slope. A plot of  $\ln(p/n_g)$  versus  $n_g$  should be linear at concentrations well above the Henry's law limit so that extrapolation of such a plot to zero-adsorbed phase concentration provides a simple method of determining the Henry constant."

Theories to predict Henry's constants based on measured values for other compounds are not well developed, especially for activated carbon, which has an amorphous structure. Similarly, the temperature dependence of the Henry's constant should follow a van't Hoff equation. However, there is no theory to predict the magnitude of the temperature dependence. Empirically, this can be done by taking equilibrium measurements at several temperatures.

## 2.2 Potential Theory Correlation.

Operation of adsorption systems for vapors using microporous adsorbents is usually concerned with high loadings to achieve efficient adsorbent usage. Under these conditions, adsorption equilibria are generally described as resulting from a pore filling (multilayer) mechanism. A useful approach to describing this behavior is based on potential theory, which relates the adsorbed phase loading to the relative pressure and incorporates the correct saturation limit described by equation 2. A characteristic curve can be used to demonstrate how this approach correlates the temperature dependence of the equilibria. In addition, other correlation terms have been proposed. The  $\beta$  term of the Dubinin-Radushkevish (DR) equation presented in Part 2 of the current series<sup>6</sup> can be used to coalesce the adsorption equilibria of many chemical compounds into a single correlation. Possible terms, which can be used for  $\beta$ , include molar volume, critical temperature, and

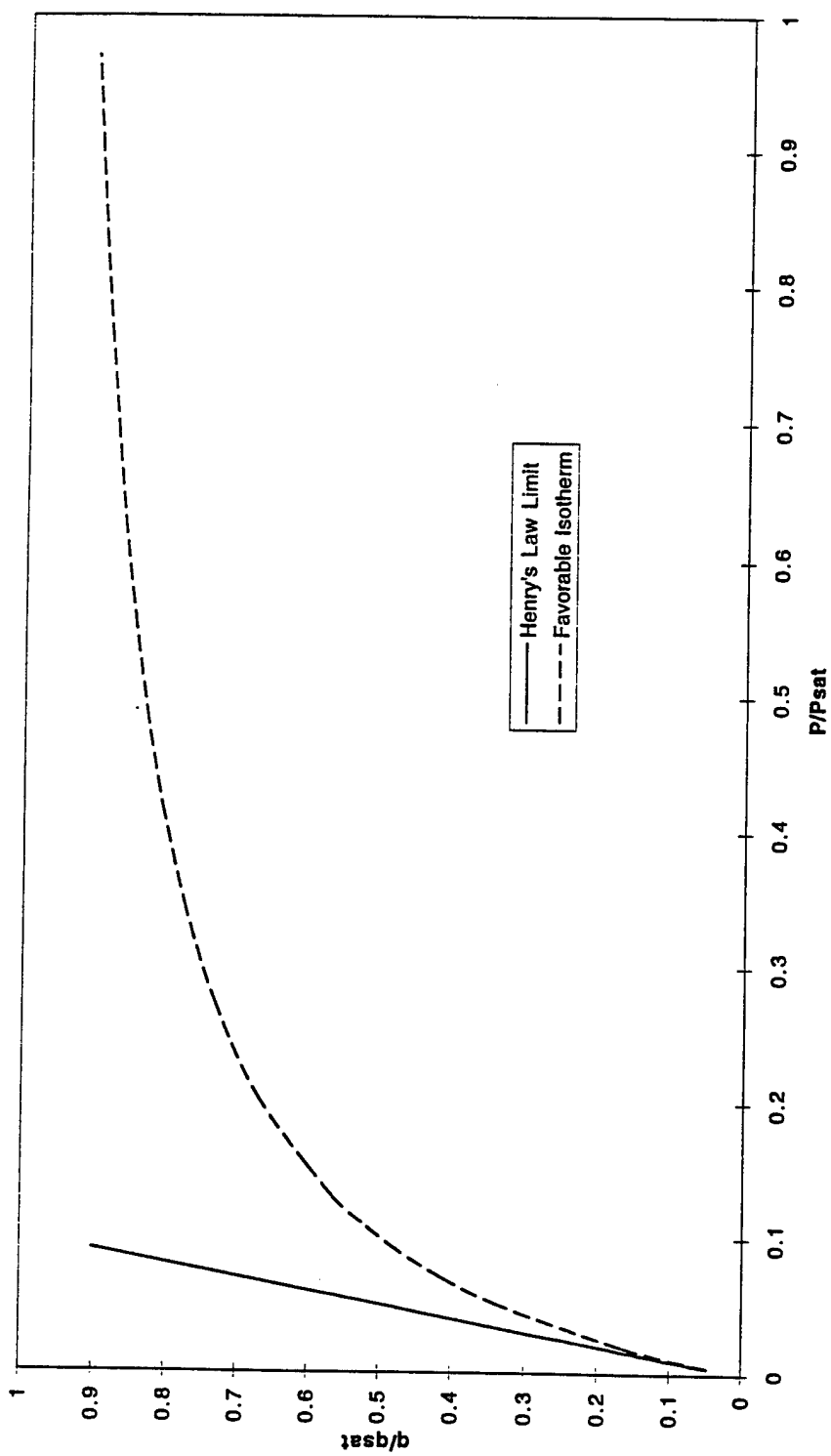


Figure 1. Representative Isotherm and Henry's Law Slope

molecular parachors. Adequate correlation using this approach for a wide range of chemicals and temperatures provides a high level of confidence for limited extrapolation beyond measured conditions.

The potential theory approach works well in predicting the saturation loading for unmeasured compounds because in the limit of  $p/p_{sat}$  approaching 1, the loading is primarily dependent on the available pore volume and the molar volume of the adsorbed phase, which is usually available in the literature. The correlation is not as accurate at low concentrations,  $p/p_{sat}$  approaching 0, because not enough information is included in the  $\beta$  term to accurately describe the adsorbent-adsorbate (monolayer) interaction. However, the largest deviations are usually noted between either small highly polar or highly non-polar species such as acetone, methanol, and hexane. Larger molecules are better described by this approach, probably because the adsorption interaction represents an average over several points of differing polarity on the molecule. In addition, for larger molecules, the vapor pressure decreases so that measuring data at low relative pressures (very low absolute pressures) is much more difficult than for higher vapor pressure compounds. The tangent limit in the Henry's law regime can be incorporated in the DR equation by correlating the data in a nonstandard approach.<sup>9</sup>

The potential theory correlation for the coconut shell char adsorbent is shown in Figure 2. The data sources are dimethylmethylphosphonate (DMMP),<sup>9</sup> both toluene and tetrafluoroethane (R-134a).<sup>10</sup> The data were measured at temperatures ranging from 25 to 200 °C. This data covers a broad range of physical properties and temperatures. The coordinates of the plot are of the type used to represent adsorption potential, where  $\beta$  is a term in the DR equation used to coalesce data for different adsorbates.

The physical properties for these compounds and the dioxins and furans are listed in Table 1. The critical properties for DMMP were estimated by Jabcock's method.<sup>11</sup> The vapor pressures of the dioxin/furans are not reported for the liquid but rather for the solid and calculated for the liquid.<sup>12</sup> For the present study, an interpolation scheme is used to calculate the temperature dependence of the vapor pressure. A two parameter Antoine equation of the form

$$\ln(p_{sat}) = A - \frac{B}{T} \quad (3)$$

is fit to the two points (1) vapor pressure at 25 °C and (2) the boiling point, where the vapor pressure is 1 atmosphere. Values at other temperatures are calculated from that fit equation. Solubility data was obtained from Reid et al.<sup>11</sup> for all except DMMP<sup>1</sup> and the dioxin/furans for which Shlu et al.<sup>13</sup> reported data.

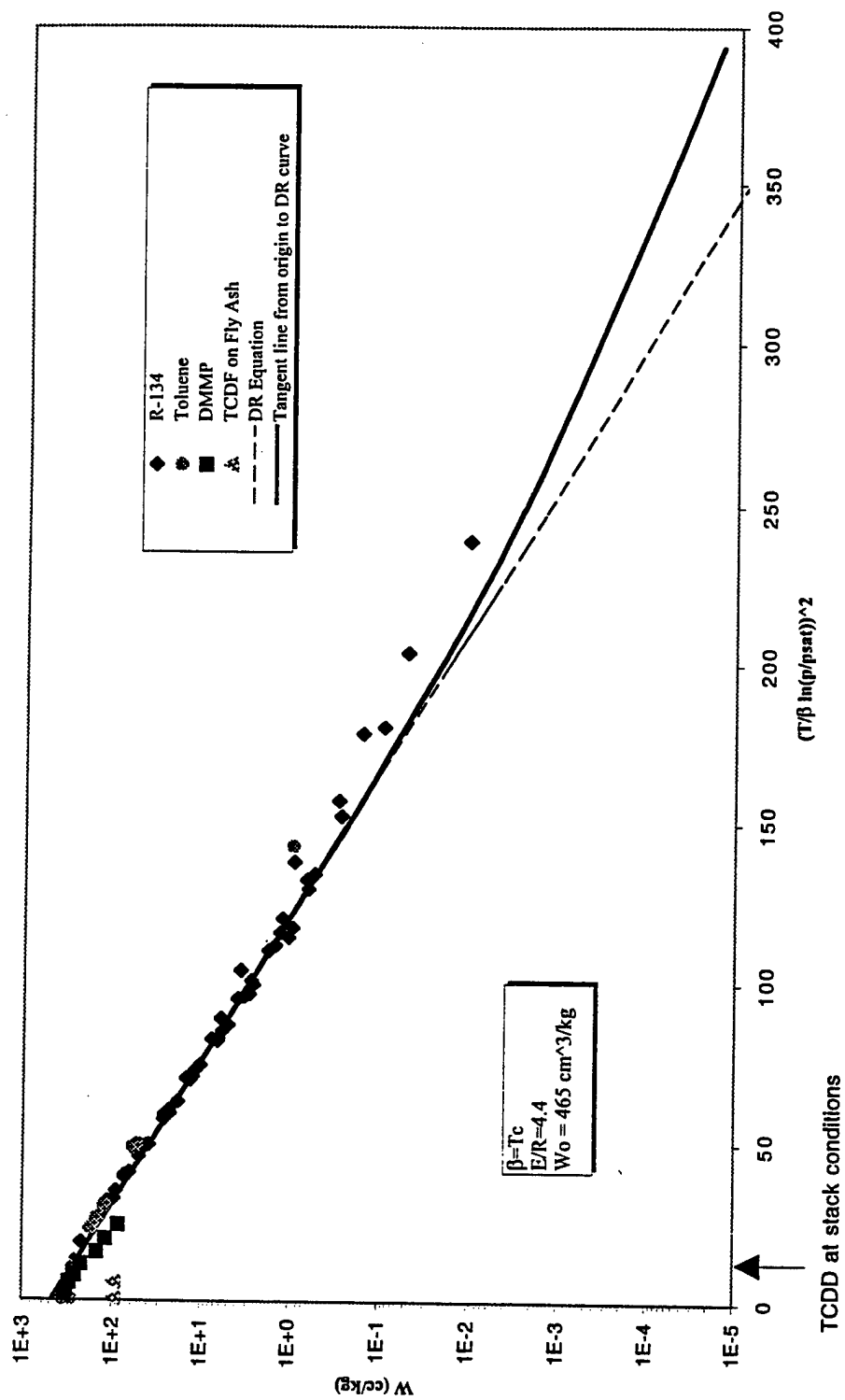


Figure 2. Potential Plot for Coconut Carbon

Table 1. Physical Properties of Adsorbable Species

	STD Vapor Pressure (Pa) 25 °C	MW	Solubility (g/L)	Tb/°C	Liquid Density (g/cm <sup>3</sup> )	Critical Temp (K)	Critical Pressure (bar)	Antoine Parameters (T in K)					Chemical Formula	
								A	B	C	D	Eqn		Pressure (units)
Toluene	3.7E+3	92.13	0.44	111	0.87	592	41	-7.3	1.38	-2.83	-2.79	1	bar	C <sub>7</sub> H <sub>8</sub>
DMMP	8.9E+1	124	inf	180	1.15	675	---	26	7010	32.42	---	3	Pa	C <sub>3</sub> H <sub>9</sub> O <sub>3</sub> P
R134a	6.6E+5	102	---	-26.5	0.8267	374	---	21.5	2211	-26.3	---	3	Pa	CHF <sub>3</sub> CH <sub>2</sub> F
TCDD	1.04E-04	322	2.00E-06	491	0.8	1029	---	---	---	---	---	---	---	C <sub>12</sub> H <sub>4</sub> Cl <sub>4</sub> O <sub>2</sub>
TDCF	1.23E-04	305	2.00E-06	464	0.8	1000	---	---	---	---	---	---	---	C <sub>12</sub> H <sub>4</sub> Cl <sub>4</sub> O

Equations are referenced in Reid et al. (Reference 10).



Based on the recorded stack concentration,  $1.17 \times 10^{-8}$  ppmv, from the JACADS facility, an adsorption potential can be calculated for TCDD. The value of this parameter,  $(T/B \ln(p/ps))^2$ , at 52 °C is 15 and is represented by the arrow on Figure 2. This suggests that the adsorption capacity is close to the saturation capacity. Data for TCDF adsorption on activated carbon has not been reported. However, there have been reported results on a fly ash.<sup>14</sup> The equilibrium partial pressure as a function of temperature was measured for a fixed loading, isostere. Several values taken from that study are shown in Table 2. This data is plotted on the potential plot. Clearly, this suggests that the measured TCDF data is in close agreement with the other simulant data. The lower capacity probably results from the low porosity of fly ash relative to activated carbon.

### 2.3 Analyzing Norit Data.

It is often possible to interpret measured adsorption data in several ways if transient behavior is masking the underlying equilibria. Recently, the separation efficiency of a carbon injection system was described for the stack gas of a municipal waste incinerator.<sup>15</sup> That report listed flowrates, carbon injection rates, temperatures, and concentrations for several facilities using injectable carbon with either a baghouse or an electrostatic precipitator. In the case of the bag house operation, an effective separation is achieved by adsorbing on the injected carbon during some contact time in the air stream. Next, the particles are captured in a thin layer built up on the fabric, which is periodically removed to prevent excess pressure drop. The electrostatic precipitator installation works in a similar way for the carbon injection, except no filter layer is formed when the particles are collected on the precipitator through which there is no flow.

It would be of interest to model the system described<sup>14</sup> to determine if the data could be described by an equilibrium model consistent with the potential relationship described earlier. If the filter train can be described as a CSTR, then a material balance on the vapor phase concentration can be written as

$$V \frac{dc}{dt} = (c_o - c)Q - k_v a(c - c^*) \quad (4)$$

The material balance on the adsorbed phase can be written as

$$m \frac{dq}{dt} = (q_o - q) \frac{m}{V} Q + k_v a(c - c^*)V \quad (5)$$

These equations can also be written as a function of the residence time,  $\tau = V/Q$ ,

$$\tau \frac{dc}{dt} = (c_o - c) - k_v a \tau (c - c^*) \quad (6)$$

Table 2. Measured Adsorption Data from Rordorf (1985)

	P (Pa)	T (C)	P <sub>sat</sub> (Pa)	T/BETA ln(p/ps) <sup>2</sup>	q (mg/g)	Liquid Density (g/cm <sup>3</sup> )	W (cm <sup>3</sup> /kg)
TCDF on Fly Ash	2.50E-05	34.7	3.64E-04	6.41E-01	75	0.8	93.75
TCDF on Fly Ash	6.30E-03	1.437E+02	2.28E+00	5.69E+00	75	0.8	93.75

$$\tau \frac{dq}{dt} = (q_o - q) + k_v a \tau (c - c^*) \frac{V}{m} \quad (7)$$

the adsorption equilibrium relates the adsorbed and vapor phase concentrations

$$c^* = f(q, T) \quad (8)$$

Three cases can be considered, linear equilibria,

$$c^* = Kq \quad (9)$$

the DR equation,

$$\ln(q / q_{sat}) = -RT / \beta E [\ln(c_s / c)]^2 \quad (10)$$

and irreversible adsorption,

$$c^* = 0.0 \quad (11)$$

To estimate the mass transfer coefficient, a correlation for a single particle was used.<sup>16</sup> The reported design parameters from Norit<sup>15</sup> are listed in Table 3. The velocity for this problem was assumed to be 56 ft/min at 130 °F, which is consistent with the stack gas carbon filter design. The term relating the surface area for diffusion to the volume, *a*, was calculated as follows.

$$\begin{aligned} a &= \text{particle area/system volume} = (\text{mass carbon/volume air}) \\ &\quad * (\text{area carbon/volume carbon}) * (\text{volume carbon/mass carbon}) \\ &= (m/V) * (3/R_p) * (1/\text{density of carbon}) \end{aligned}$$

The particle size was given to be no greater than 325 mesh (2e-5 m).

Table 3. Norit Dioxin Filtration Parameters

temperature (°C)	132
density of carbon (g/cm <sup>3</sup> )	1.0
superficial velocity (m/s)	0.4
particle radius (cm)	2e-4
diffusivity in air (cm <sup>2</sup> /s)	0.2
density of air (g/cm <sup>3</sup> )	8.4e-3
viscosity of air (Pa s)	2.3e-5
Re	0.06
Sc	1.36
Sh	2.0
kv (cm/s)	1000

Equations 6-8 were solved numerically using a differential equation solver. The input values are the quantity  $m/V$ ,  $k_v a^* \tau$ ,  $C_{feed}$ ,  $q_o$  and the isotherm choice. The slope of the linear isotherm,  $K$ , was calculated from a line between the origin and the loading calculated from the inlet and outlet concentration difference divided by the carbon mass. The reported measured concentrations for four cases together with calculated loading are presented in Table 4.

Table 4. Norit Dioxin Filtration Case Results

	A	B	C	D
$m/V$ (mg/DSCM)	362	322	116	291
$a$ (cm <sup>-1</sup> )	5.4e03	4.8e-3	1.73e-3	4.3e-3
$C_{in}$ (ng/DSCM) *	128	411	416	94
$C_{out}$ (ng/DSCM) *	4.6	16	6	2
$q_{calc}$ (ng/mg)	0.34	1.2	3.5	0.31
$K$ (ng/m <sup>3</sup> )/(ng/mg)	13.5	13.3	1.7	6.45

\*C represents total of CDD + CDF

Tables 5 and 6 present model calculations where the parameter  $k_v a^* \tau$  is varied. The effect of increasing  $k_v a^* \tau$  for a constant value of  $k_v a$  is to simulate operation of the CSTR for a longer residence time. Eventually, a steady state is approached. Steady state is achieved first by the linear, then by DR, and finally by the irreversible isotherms. The predicted differences of performance for cases A and B is small among the three isotherms at contact times consistent with a real system.  $k_v a^* \tau$  of 2 and 20 correspond to contact times of 0.4 s and 4 s, respectively. Even at  $k_v a^* \tau$  of 200 (a 40 s) contact time, the difference in predicted outlet concentration for each isotherm shape is not different enough

Table 5. Case A - CSTR Simulation of Norit Data

Isotherm Shape	Tau *kva = 2	Tau *kva = 20	Outlet Concentration (ng/m <sup>3</sup> )		
			Tau *kva = 200	tau *kva = 2e4	tau *kva = 2e9
Linear DR Irreversible	44	10	5	4.7	4.7
	42	6	0.6	6.0E-3	7.9E-6
	42	6	0.6	6.0E-3	6.0E-6
Concentration Inlet = 128 ng/m <sup>3</sup>					
m/V (mass carbon/volume air is given) = 362 mg/m <sup>3</sup>					
Measured Outlet Concentration = 4.5 ng/m <sup>3</sup>					

18

Table 6. Case B - CSTR Simulation of Norit Data

Isotherm Shape	Tau *kva = 2	Outlet Concentration (ng/m <sup>3</sup> )	
		Tau *kva = 20	Tau *kva = 200
Linear DR Irreversible	144	34	19
	137	19	2
	137	19	2
Concentration Inlet = 411 ng/m <sup>3</sup>			
m/V (mass carbon/volume air is given) = 322 mg/m <sup>3</sup>			
Measured Outlet Concentration = 16 ng/m <sup>3</sup>			

to confidently conclude that the data could only be represented by one of the isotherm models. This result suggests that mass transfer limitations are contributing significantly to the observed results.

An analytical solution of the outlet concentration for equations 6-8 can also be obtained for the case of an irreversible isotherm.

$$C = \frac{C_o}{(kva\tau + 1)} [1 + kva\tau \exp(-(kva\tau + 1)t)] \quad (12)$$

Clearly, for either long contact times or large mass transfer rates, the outlet concentration tends to zero. With small values for the contact time and the mass transfer coefficient, the solution indicates that finite concentrations can be seen in the product even for an irreversible isotherm.

#### 2.4 Applying Raoult's Law to Post-Treatment Filter.

Raoult's law was originally developed to describe the vapor-liquid equilibria of ideal mixtures, which are formed of components with similar properties. Liquid mixtures of water and nonwater soluble substances are highly nonideal. Raoult's law was later adapted for use in describing adsorbed solutions. The formulation used in the current model is

$$P_i = x_i P_i^o(\theta^o) \quad (13)$$

$$\theta^o = \sum_{j=1}^{n_a} \theta_j \quad (14)$$

where  $P_i$  is the vapor pressure of the  $i$ th adsorbate,  $x_i$  is the mole fraction of the adsorbed phase species "i," and  $P_i^o$  is the pressure predicted from the isotherm at the fractional loading of the mixture,  $q_j$ . Equation 13 becomes identical to Raoult's law for vapor-liquid equilibrium expression when the sum of the fractional loadings is unity (when the adsorbent is saturated), provided the adsorption equilibrium expression reduces to the vapor pressure equation. The condition is satisfied by pore filling models such as the D-R equation.

Four cases must be considered for applying Raoult's law for adsorption: organic/organic (high concentration), organic/water (high organic concentration), organic/organic (low concentration), and organic/water (low organic concentration). Investigations show that Raoult's law gives accurate predictions of organic/organic multicomponent

breakthrough behavior at high adsorbed phase concentrations. But, the results are strongly dependent on the use of accurate isotherm data. This was demonstrated in the filter model report for breakthrough under dry conditions for acetone and hexane on BPL carbon.<sup>7</sup> In the case of organic/water adsorption, the Raoult's law approach predicted that the coadsorption of water had a larger effect on the organic loading than the effect observed in the data. This is illustrated in the model report for acetone/hexane breakthrough under humid conditions, the Raoult's predictions of the hexane/water equilibria data of Rudisill,<sup>17</sup> and the eight component breakthrough experiments under humid conditions. This is consistent with the Raoult's law approach of volume filling because water is only weakly adsorbed by a capillary condensation mechanism, while the organics are more strongly adsorbed consistent with favorable adsorption. Thus, although Raoult's law is in error for high water loading, the error is consistent and conservative in that it overpredicts the ability of water to compete with organics for adsorption sites.

In the limit, as total loading approaches zero, individual components of adsorbed mixtures should behave independently, with each component adsorbing according to its Henry's law limit. Studies show that the Raoult's law model only approaches this correct limit when volume fractions, not mole fractions, are used.<sup>17</sup> However, in the present work, Raoult's law based on mole fractions describes the measured data better than volume fractions. This is because of the large difference in molar volume between water and the organics. If the molar volumes of the organics are similar, the difference between predictions based on mole fractions and volume fractions is also small. If the differences in molar volumes of the organics are large, the difference between predictions based on mole fractions and volume fractions would increase. However, large differences in vapor pressure would likely contribute most to the relative adsorption affinity. Thus, because of (1) the better agreement with the data using mole fractions, (2) the fact that Manes original development used mole fractions, and (3) the predicted loadings of the HRA compounds are outside the Henry's law regime, Raoult's law based on mole fractions is considered appropriate.

The effect of high fractional loadings of adsorbed water on the adsorption of organics at low fractional loadings can be addressed. Data was presented in the report for breakthrough at high organic and water loadings. Experimental difficulties at low concentrations and loadings severely limit the ability to measure data in this regime. The trends observed in the data are expected to be similar at the lower organic concentrations, that is overpredicting the influence of water. In fact, the trend at low loading would be for even greater overprediction because the small amount of organic adsorbed at low concentrations is in reality more strongly adsorbed than at high concentrations. But, Raoult's law does not account for this effect, because the pure component partial pressure is dominated by  $\Theta$ , which becomes independent of the organic component at low organic loadings. Therefore, the model becomes more conservative with lower adsorbed phase organic loadings.

A review of reported multicomponent adsorption equilibrium theory is required to identify the best current approaches and possible focus of future development for the pollution abatement system (PAS) carbon filter performance model. The main criteria for

inclusion in the model would be correct predictions of many component organic-organic interaction, organic-water interaction, and that the solution be appropriate for inclusion in a fixed bed model, i.e., minimal amount of iteration.

Many of the most frequently cited theories require that each component in the mixture have a Type I isotherm. Water adsorption on carbon does not meet this criterion. This then rules out all the extensions of the Langmuir model for this problem. The Ideal Adsorbed Solution (IAS) Theory and Vacancy Solution Model (VSM) are developed from an initial premise that the adsorbed mixture forms a single ideal phase. However, the latter has been shown to not meet the thermodynamic consistency requirements. The former has also been shown to have the restriction on its application near the saturation regime. Doong and Yang<sup>18</sup> proposed a pore filling model for mixed organic water adsorption, which was largely empirical, fit the data well, but was not defined for components with differing pure component pore volumes. Grant and Manes<sup>19</sup> extended the Polanyi pore filling concept to mixtures by equating the chemical potentials for equal volumes adsorbed. The predictive abilities of the potential theory and the ideal adsorbed theory are comparable. Thus, the IAS and the single adsorbed phase potential theory give safe-sided predictions of the effect water has on adsorption of nonwater soluble components. Water is predicted to be adsorbed as strongly as the organic phase; in reality, it is not. Thus, a breakthrough model based on this assumption must predict that the organics are displaced sooner than observed. Clearly, more work is required in this area.

Manes<sup>20</sup> has extended the potential theory to a two-phase system. For some substances, the two-phase theory makes predictions that are substantially better than IAS and the single phase potential theory (Raoult's Law). For soluble substances, predictions are not improved. As used in the PAS filter model, the single phase potential theory was found to give predictions accurate to within the errors introduced by the single component isotherms below about 80% - 90% RH. When RH exceeds this level, errors due to the Raoult's Law become dominant. Incorporating a two-phase potential theory model may increase the accuracy of the model predictions, but it can be confidently predicted that this more accurate model will predict later breakthrough for all the insoluble species. The magnitude of the correction would have to be calculated for each case.

### 3. CONCLUSIONS

An analysis is presented to predict an extremely efficient removal of dioxin and furans for the entire life of the post-treatment filter.

A methodology is proposed to estimate the adsorption capacity of low-concentration, high boiling compounds on activated carbon. A Henry's Law limit is proposed for the Dubinin-Radushkevich equation, which retains all the inherent advantages of simplicity and convergence stability.

Available data for dioxin adsorption on activated carbon was reconciled with potential theory models by use of simple equilibrium and a rate-based CSTR model.



**Blank**

## GLOSSARY

$a$	= particle area-to-volume ratio
$c$	= vapor phase concentration
$c_{sat}$	= saturation vapor phase concentration
$k_v$	= mass transfer coefficient
$m$	= mass of adsorbent injected
$Q$	= volumetric flowrate of air
$q$	= solid phase concentration (mol/kg)
$T$	= temperature (K)
$V$	= volume of carbon injection system
$V_m$	= molar volume (cm <sup>3</sup> /mol)
$x$	= solid phase mole fraction

### Greek Symbols

$\beta E$	= energy term for DR equation
$\varepsilon$	= adsorption potential
$\Theta$	= fractional loading
$\tau$	= residence time

Blank

## LITERATURE CITED

1. PFS Alternative Configuration Study, Contract No. DACA 87-86-C-0084, Task No. B-11E1, Ralph M. Parsons, Incorporated, Pasadena, CA, June 1995, UNCLASSIFIED Report.
2. Results of the RCRA Trial Burn with VX Feed for the Liquid Incinerator at the Johnston Atoll Chemical Agent Disposal System, Contract No. DACA87-86-C-0098, SRI-APC-92-384-7350.11.1-I-R3, Southern Research Institute, Birmingham, AL, June 1991, UNCLASSIFIED Report.
3. Results of the RCRA Trial Burn for the Liquid Incinerator at the Johnston Atoll Chemical Agent Disposal System, Contract No. DACA87-86-C-0098, SRI-APC-91-190-6967-006-F-R4, Southern Research Institute, Birmingham, AL, June 1991, UNCLASSIFIED Report.
4. Goldfarb, A., Anderson, G., Mahle, J., and Croft, D., Pollution Abatement System Carbon Filter Simulation Model Development, Contract No. DAAM01-95-D-002, Mitretek, Incorporated, McLean VA, November 1996, UNCLASSIFIED Report.
5. Mahle, J., Buettner, L., and Mauer, S., Evaluation of the Post-Treatment Filter, Part 1: Experimental Study of DMMP and DIMP Filtration at High Temperature and High Dew Point Using Activated Carbon, ERDEC-TR-317, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, December 1996, UNCLASSIFIED Report.
6. Croft, D., Friday, D., and Mahle, J., Evaluation of the Post-Treatment Filter, Part 2: Modeling Laboratory-Scale Filter Breakthrough Data, ERDEC-TR-317, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, December 1996, UNCLASSIFIED Report.
7. Croft, D., Friday, D., and Mahle, J., Evaluation of the Post-Treatment Filter Part 3: Multicomponent Breakthrough Data, ERDEC-TR-317, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, August 1997, UNCLASSIFIED Report.
8. Ruthven, D.M., Principles of Adsorption and Adsorption Processes, pp 48-49, 68-70, John Wiley and Sons, New York, NY, 1984.
9. Mahle, J.J., "A Henry's Law Limit for the DR and DA Equations," Carbon Vol. 35 (3), p 432 (1997).
10. Croft, D.T., and Mauer, S.M., Adsorbent Evaluation and Adsorption Equilibrium Data for R-123, R-134a, and Toluene on Selected Activated Carbons, Silica Gels, and Polymeric Resins, ERDEC-CR-227, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, July 1997, UNCLASSIFIED Report.

11. Reid, R., Prausnitz, J., and Poling, B., The Properties of Gases and Liquids, 4th ed., pp 14-15, 657, McGraw Hill, Incorporated, New York, NY, 1987.
12. Rordorff, B.F., "Thermal Properties of Dioxins, Furans and Related Compounds," Chemosphere Vol. 15 (9-12), p 1325 (1986).
13. Shlu, W.Y., Doucette, W., Gogas, F., Andrean, A., and MacKay, D., "Physical-Chemical Properties of Chlorinated Dibenzo-p-dioxins," Environ. Sci. Tech. Vol. 22 (6), p 651 (1988).
14. Rordorff, B.F., "Thermodynamic and Thermal Properties of Polychlorinated Compounds: The Vapor Pressures and Flow Tube Kinetics of Ten Dibenzo-Para-Dioxins," Chemosphere Vol. 14 (6), p 885 (1985).
15. Norit Activated Carbons for the Removal of Mercury and Dioxin from Flue Gas, Report 74-3, Norit America's, Incorporated, Atlanta, GA, undated.
16. Geankopolis, C.J., Transport Processes and Unit Operations, 2nd ed., Allyn and Bacon, Boston, MA, 1983.
17. Rudisill, E.N., Studies on Water-Hydrocarbon Adsorption Equilibria and Adsorptive and Membrane Separations, PhD Thesis, University of Virginia, Charlottesville, VA, May 1991.
18. Doong, S.J., and Yang, R.T., "Adsorption of Mixtures of Water Vapor and Hydrocarbons by Activated Carbon Beds: Thermodynamic Model for Adsorption Equilibrium and Adsorber Dynamics," AIChE Symp. Ser. Vol. 83 (259), p 87 (1988).
19. Grant, R.J., and Manes, M., "Adsorption of Binary Hydrocarbon Gas Mixtures on Activated Carbon," I&EC Fundamentals Vol. 5 (4), p 490 (1966).
20. Manes, M., "Estimation of the Effects of Humidity on the Adsorption onto Activated Carbon of the Vapors of Water-Immiscible Organic Liquids," In Fundamentals of Adsorption, p 335, A.L. Meyers and G. Belfort, Eds., Engineering Foundation, New York, NY, 1983.